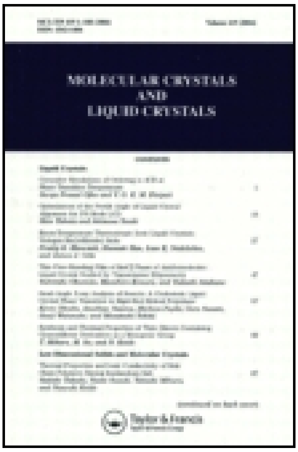

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# Novel Blue Organic Light Emitting Materials

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# Novel Blue Organic Light Emitting Materials

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The new blue light emitting materials containing anthracene were designed, synthesized and characterized. The materials were prepared in high yields by well-known reactions such as Grignard reaction, synthesis of boronic acid, and Suzuki coupling reaction. The non-coplanar structures of materials were confirmed by using the PM3 parameterization in the Hyper Chem 5.0 program (Hypercube) in order to fully optimize the structure of molecule. The obtained materials showed a thermal stability and a good film forming ability. It is found that the energy transfer from substituents to anthracene took place effectively.

Keywords: Blue light emitting materials; Antracene; Suzuki coupling; Non-coplanar structure; Good film forming ability; Energy transfer

## INTRODUCTION

Organic electroluminescent devices have been widely investigated for their applications in full-color flat panel displays. Ever since Tang and Van Slyke reported the first double-layer green thin-film organic electroluminesent device [1], light emitting materials, device configuration, and electrode materials have been studied to improve the efficiency and stability of the organic EL devices. One attractive way to improve EL efficiency is to find some means to increase the luminescence efficiency of emitter. The EL colors of their devices could be readily tuned from blue-green to orange red. However, for a full color display, three basic colors, red, green, and blue, are needed. Compared with green emitting devices, the EL characteristics of blue and red emitting ones have to be improved particularly in terms of color purity and efficiency for full color application [2]. It is much more difficult to emit a pure blue light due to the excimer emission and its intrinsic characteristic of having a wide band-gap irrespective of the type of materials. In spite of several reports on the blue OELD, only a limited number of materials are practically applicable in terms of brightness and stability. Related to phenylenevinylene is 4,4'-bis(2,2-diphenylvinyl)biphenyl(DPVBi) developed by the Idemitsu Kosan Company, which has a glass transition temperature below 100°C. Although the blue-emitting devices based on DPVBi derivatives achieved a high luminous efficiency of 6 lm/W in a doped configuration, its color chromaticity indicated a bluish-green emission, not pure blue. As a blue light-emitting organometallic quinoline complex, bis(8-hydroxyquinaldine) aluminum phenoxide ($Alq_2OPh$) and bis(8-hydroxyquinaldine) aluminum biphenoxide (BAlq) were reported by Eastman Kodak. Other organometallic complexes emitting blue light include benzoxazole derivatives such as bis[2-(2-hydroxyphenyl)benzoxazolato] zinc [$Zn(BOX)_2$ or $Zn(Oxz)_2$], and tris[2-(2-hydroxyphenyl)-benzoxazolato] dizinc(II) chloride [$Zn_2(Oxz)_3Cl$]. However, it has been reported that these zinc benzoxazole complex derivatives are not stable enough to use as blue emitters in practical applications [3].

In the present work, we report on the design, synthesis, and characterization of blue light emitting materials, containing anthracene which is highly fluorescent and efficient chromophore. Based on the anthracene, bulky noncoplanar groups were introduced. The newly synthesized anthracene based blue emitting materials are expected to be stable and efficient.

## EXPERIMENTAL

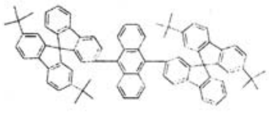
Elemental analyses, $^1$H-NMR and $^{13}$C-NMR spectra, thermogravimetric analysis, differential scanning calorimetry were performed as reported previously. Synthesis of materials are reported elsewhere [4]. The stereostructure of the synthesized molecules is calculated by using the PM3 parameterization in the HyperChem 5.0 program (Hypercube) in order to fully optimize the structure of molecule. EL spectra of the devices were measured utilizing a diode array rapid analyzer system (Professional scientific instrument Corp.). Fluorescence spectra of blue emitting materials in chloroform solution and solid state were measured using a spectrofluorometer (Shimadzu Corp.)

## RESULTS AND DISCUSSIONS

For the synthesis of 9,10-bis(naphtyl)anthracene (BNAn), 9,10-bis(4'-triphenylsilylphenyl)anthracene (TPSiDPA), and 9,10-bis(2'7'-di-t-butylspirobifluorenyl)anthracene (TBSA), the Suzuki coupling reaction was employed. The structures are sketched in scheme 1. The molecular structure of obtained materials was confirmed by FT-IR and $^1$H- and $^{13}$C-NMR spectroscopy and elemental analysis.

Bis-9,10-(1'-naphthyl)anthracene

Bis-9,10-(4'-triphenylsilylphenyl)anthracene



Bis-9,10-(2',7'-di-t-butylspirobifluorenyl)anthracene

SCHEME 1. The structures of the synthesized materials

In order to optimize the molecular structure of pure blue emitting materials, the stereostructures of the synthesized materials were theorectically characterized by using the PM3 parameterization in the Hyper Chem 5.0 program (Hypercube) (Figure 1).

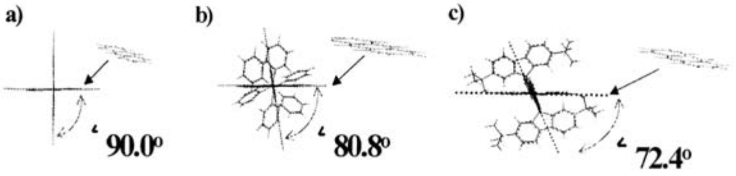


FIGURE 1. The stereostructures of the synthesized materials, BNAN(a), TPSiDPA(b), TBSA(c)

In the case of BNAn, naphtyl group is highly twisted toward anthracene moiety, and twisting angle reaches to about 90 degrees. It is calculated that the twisting angles are about 80.8 $^{0}$ and 72.4 $^{0}$ in TPSiDPA and TBSA, respectively.

The obtained materials showed good solubility in common organic solvents. The synthesized materials had good film forming ability and offer smooth and flat thin films without any pin-holes by thermal evaporation. This may be due to the molecular conformation of materials which are designed as having non-coplanarity and low intermolecular interaction. The thermal property of the synthesized molecules was evaluated by means of TGA in a nitrogen atmosphere. The weight losses of the BNAn, TPSiDPA, TBSA begin at 350 °C, 450 °C and 420 °C, respectively. We can not find the glass transition temperature of BNAn and TPSiDPA until reaching to 300 °C in differential scanning calorimetry (DSC). In the case of TBSA, the glass transition temperature is around 207 °C. The results show that the molecules have good thermal stability even though they are low molecular weight organic compounds. It is supposed that the introduction of bulky non-coplanar substituents into a rigid anthracene center allows the ability to form a thermally stable amorphous film. Stability in the amorphous state is a basic requirement for materials used in LED, since, generally, aggregation and microcrystallization have detremental effects on the device stability.

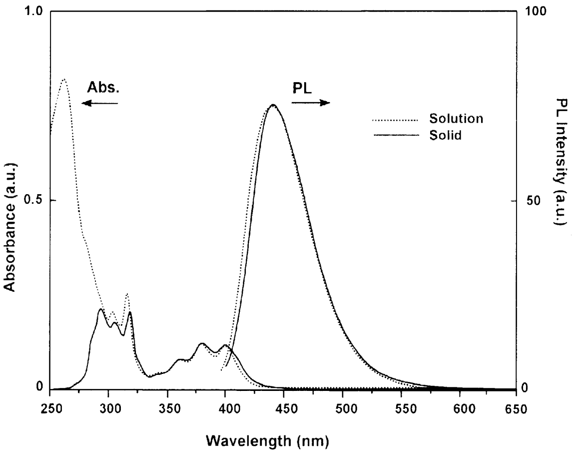


**FIGURE 2. The UV visible and PL of the TBSA**

Figure 2 shows the optical absorption and photoluminescence spectra of a dilute solution of TBSA in chloroform and thin film of TBSA by thermal evaporation. The UV-vis optical absorption of TBSA shows the characteristic vibrational pattern of the isolated anthracene group ($\lambda_{max}$ = 344, 363, 382, 403 nm) and spirobifluorene group ($\lambda_{max}$ = 320) both in solid state and dilute solution. The similarity between the absorption spectra of a dilute solution and a thin film suggests that the conformation of the solid state of TBSA is similar with that of the solution state of TBSA, which is attribute to its non-coplanar structure. The photoluminescence spectra of the dilute solution of the TBSA pumped by UV light ($\lambda$ = 320 nm, 363 nm, 382 nm) have a maximum peak at 442 nm. It means that energy transfer from spirobifluorene to anthracene occurred effectively. Therefore, it is expected that TBSA is efficient emitting material. The thin film and dilute solution of TBSA showed similar blue PL with an emission maximum at 442 nm and 443 nm, respectively. We can not find any shoulder emission peak due to excimer formation which usually appears in a PL spectrum of thin films with a planar structure of molecules. It is strongly suggested that intermolecular interaction is almostly supressed. The similar results were also observed in anthracene based new emitting materials, BNAn and TPSiDPA. Electroluminescent characteristics of the devices are fabricated from BNAn, TPSiDPS, and TBSA will be reported elsewhere.

**Acknowledgments**
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